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Application of Colloid Probe Atomic Force Microscopy to the Adhesion of Thin Films of Viscous and Viscoelastic Silicone Fluids

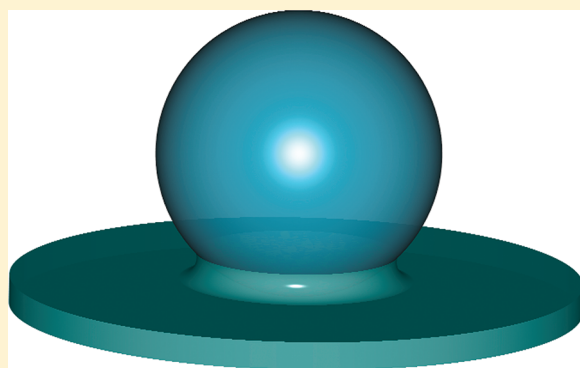
James Bowen,[†] David Cheneler,[‡] James W. Andrews,[†] Andrew R. Avery,[§] Zhibing Zhang,[†] Michael C. L. Ward,[‡] and Michael J. Adams^{*,†}

[†]School of Chemical Engineering and [‡]School of Mechanical Engineering, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

[§]Unilever R&D Port Sunlight, Quarry Road East, Bebington, Wirral CH63 3JW, United Kingdom

 Supporting Information

ABSTRACT: The adhesive characteristics of thin films (0.2–2 μm) of linear poly(dimethylsiloxane) (PDMS) liquids with a wide range of molecular weights have been measured using an atomic force microscope with a colloid probe (diameters 5 and 12 μm) for different separation velocities. The data were consistent with a residual film in the contact region having a thickness of ~ 6 nm following an extended dwell time before separation of the probe. It was possible to estimate the maximum adhesive force as a function of the capillary number, Ca , by applying existing theoretical models based on capillary interactions and viscous flow except at large values of Ca in the case of viscoelastic fluids, for which it was necessary to develop a nonlinear viscoelastic model. The compliance of the atomic force microscope colloid beam was an important factor in governing the retraction velocity of the probe and therefore the value of the adhesive force, but the inertia of the beam and viscoelastic stress overshoot effects were not significant in the range of separation velocities investigated.



1. INTRODUCTION

There are many examples for which the adhesion associated with liquid junctions between solid surfaces is important, such as granular materials,^{1–3} hard disk drives,^{4–6} nanotribology,^{7,8} nanolithography processes,^{9,10} and in the interaction of particles within the lungs.^{11–13} Under static conditions, the adhesion arises from capillary attraction while viscous forces will also be developed when there is relative motion between the solid surfaces. Liquid bridges have been studied theoretically by numerous researchers, and also experimentally often with water or another Newtonian fluid. For example, atomic force microscopy (AFM) has been employed widely to investigate the capillary forces,¹⁴ including the effect of humidity on condensed bridges for hydrophilic and hydrophobic systems,^{15–17} the critical effect of tip geometry on the magnitude of the forces and the rupture stability,^{18,19} assessing the geometry of nanoscale contacts,²⁰ and the stability of nanoscale aqueous liquid bridges taking into account possible effects arising from cavitation.²¹ The influence of surface wetting on the capillary forces between solid planar surfaces has been considered for both aqueous and nonaqueous systems.^{22,23} For rigid spheres, analytical and closed-form approximations have been developed for the capillary interactions^{15,24–26} and also the viscous force in the lubrication limit.^{27–29} Non-Newtonian fluids have been considered primarily for polymeric systems, when it is possible to approximate the flow behavior by a power-law relationship.³⁰ The effect of non-Newtonian flow on

the separation of a sphere from a flat surface has been investigated,³¹ in which the analytical solution derived by Streator³² provided a lower bound for the separation time.

The current work involves the measurement of adhesion, at small separation distances in the vicinity of the peak adhesive force, using colloid probe AFM for thin films of a range of Newtonian and viscoelastic poly(dimethylsiloxane) (PDMS) liquids deposited on Si wafers. The detachment of a spherical probe from thin Newtonian liquid films has been considered previously using a pendulum,³³ a load cell,³⁴ and AFM.³⁵ The current work builds on the previous research by considering the total viscous and capillary contributions to the measured force, as well as interpreting the experimental data by extending existing theoretical models to account for linear and nonlinear viscoelasticity including stress overshoot. The validity of the models is evaluated by comparison with the experimental data.

2. THEORETICAL

In this section, theoretical models are described for calculating the adhesive force developed during the separation of a liquid junction. They are based on the system geometry that is shown in Figure 1 for a colloid probe in contact with a liquid film deposited on a smooth planar surface

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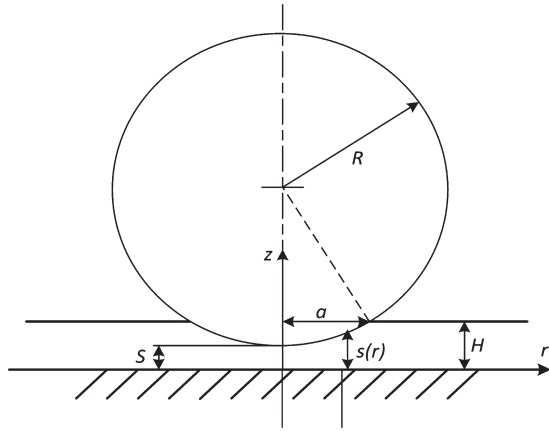


Figure 1. Sphere-on-flat geometry for a film thickness H .

such that the location of the three-phase contact line defining the liquid contact radius, a , is approximated by ignoring the meniscus. The axial and radial coordinates, (z, r) , are also shown with an origin on the planar surface. The gap between the colloid probe and the planar surface, $s(r)$, has a minimum value $s(0) = S$. The models assume that the adhesive force is the sum of the capillary attraction and that associated with shear flow in the lubrication limit. Numerical models involving extensional flow terms are required at larger separation distances and will not be considered in the current work.

2.1. Capillary-Viscous Model. Matthewson³³ proposed that the total force, F , acting on a sphere of radius R , when partially immersed in a perfectly wetting thin film of a Newtonian liquid and with a separation velocity, \dot{S} , is the sum of the capillary, F_C , and viscous forces, F_V , thus

$$F = F_C + F_V \quad (1)$$

where

$$F_C = 4\pi\sigma R \left(1 - \frac{S}{H}\right) \quad (2)$$

and

$$F_V = 6\pi\eta R^2 \left(1 - \frac{S}{H}\right)^2 \frac{\dot{S}}{S} \quad (3)$$

and where σ is the surface tension, H is the film thickness, and η is the viscosity of the liquid. The second term in eq 1 assumes that the lubrication approximation is valid and that there is a no slip boundary condition. For the current system, the first assumption is valid since data analysis is restricted to minimum separation distances between the colloid probe and the Si wafer that are at least an order of magnitude smaller than the wetted contact radius of the probe ($a \gg S$). The no slip condition will be discussed in section 5.5. The first-order expression for the capillary force (eq 2) was employed rather than obtaining a closed-form approximation to a numerical solution of the Young–Laplace equation because the solution is degenerate for this particular geometry of sphere-on-thin film due to the radius of the meniscus at the liquid film/air interface being singular.³⁶

Since the force acting on the probe is due to the deflection of the AFM cantilever, it is necessary to account for the beam stiffness or spring constant, k , as follows:

$$F = k[Vt - (S - S_0)] \quad (4)$$

where V is the drive velocity of the fixed-end of the AFM cantilever and S_0 is the minimum separation distance at $t = 0$ corresponding to the time, t , at which retraction of the probe is initiated following the dwell period.

Equating eqs 1 and 4 and including the possible effect of the acceleration of the probe, and assuming the effect of fluid inertia to be small in comparison, the resulting equation of motion may be written in nondimensional form as follows:

$$F^* = \frac{F}{4\pi\sigma R} = \frac{k}{4\pi\sigma R} [Vt - (S - S_0)] \\ = \left(1 - \frac{S}{H}\right) + \frac{3\eta R}{2\sigma} \left(1 - \frac{S}{H}\right)^2 \frac{\dot{S}}{S} - \frac{m\ddot{S}}{4\pi\sigma R} \quad (5)$$

where m is the total effective mass of the AFM beam assembly and \ddot{S} is the acceleration of the probe. The effective mass is the sum of the mass of the colloid probe, m_c , and the effective mass of the cantilever beam, m_b . For the rectangular cross-section beams used in the current work, m_b may be determined on the basis that the deflection of a cantilever under point loading at the free end may be closely approximated by the first mode shape of an oscillating cantilever, thus³⁷

$$m_b = 0.97k \frac{L^4 \rho_b}{d^2 E} \quad (6)$$

where L , d , ρ_b , and E are the length, thickness, density, and Young's modulus of the beam. Hence, the total effective mass may be written as

$$m = m_b + \frac{4}{3} \pi \rho_c R^3 \quad (7)$$

where ρ_c is the density of the colloid probe.

2.2. Capillary-Linear Viscoelastic Stress Overshoot Model.

Leider and Bird³⁸ considered the effects of viscoelasticity in constant force squeeze flow and suggested that the following constitutive equation is appropriate for describing transient experiments:

$$\tau + \frac{\lambda D\tau}{Dt} = -\eta_0 \dot{\gamma} \quad (8)$$

where τ is the shear stress, λ is a time constant, η_0 is the shear viscosity at a zero strain rate, $\dot{\gamma}$ is the strain rate, and D/Dt is the Jaumann's or corotational derivative. They found that it was not possible to obtain an analytical solution to eq 8 for the case of constant force and suggested an approximate solution that may be written in the following form:

$$\tau = \eta \dot{\gamma} \left[1 - e^{(-t/\lambda)}\right] + \eta \dot{\gamma}^2 t e^{-t/\lambda} \quad (9)$$

where

$$\dot{\gamma} = \frac{\partial v_r}{\partial z} \quad (10)$$

and where v_r is the radial component of the velocity and z is the axial direction of the flow field.

The first term in eq 9 is equivalent to the response for separation at a constant strain rate such that the stress at $t = 0$ is zero and increases with increasing time to an asymptotic value corresponding to a Newtonian fluid with the same zero shear rate viscosity. The second term is the response due to a sudden initiation of motion, which is defined as stress overshoot. It can be seen that the initial value of this expression is zero but becomes significant when $t \sim \lambda$ before decaying toward zero as $t \rightarrow \infty$. This second component would always be always positive regardless of the direction of motion of the probe; that is, it is path independent, whereas the sign of the first component depends on the velocity so that it is path dependent.

Neglecting inertial and extensional terms, the momentum equation for radial incompressible flow reduces to the lubrication approximation:

$$\frac{\partial P}{\partial r} = \frac{\partial \tau}{\partial z} \quad (11)$$

where P is the pressure distribution in the fluid.

It has been shown that, to first order, the elasticity of a fluid has a negligible effect on the velocity field during squeeze flow³⁹ and therefore it will be taken to be equal to that for a Newtonian fluid with a no slip boundary condition:⁴⁰

$$v_r = \frac{3rz(r)[s(r) - z(r)]\dot{s}}{[s(r)]^3} \quad (12)$$

where $s(r)$ is given by the parabolic approximation in the region $0 \leq r \leq a$:

$$s(r) = S + \frac{r^2}{2R} \quad (13)$$

Combining eqs 9–13 and integrating gives the pressure distribution as

$$P = \frac{3\dot{S}\eta}{s(r)^3} (1 - e^{-t/\lambda})(r^2 - a^2) + 3\dot{S}\eta e^{-t/\lambda} \left[\left\{ \left(2a\sqrt{SR}[15a^6 + 110a^4SR + 292(aSR)^2 - 120(SR)^3] + 15\sqrt{2}(a^2 + 2SR)^4 a \tan(a/\sqrt{2SR}) \right) / (6144(SR)^{7/2}(a^2 + 2SR)^4) \right\} - \left\{ \left(2r\sqrt{SR}[15r^6 + 110r^4SR + 292(rSR)^2 - 120(SR)^3] + 15\sqrt{2}(r^2 + 2SR)^4 a \tan(r/\sqrt{2SR}) \right) / (6144(SR)^{7/2}(r^2 + 2SR)^4) \right\} \right] \quad (14)$$

where a is given by

$$a = [2R(H - S)]^{1/2} \quad (15)$$

The resultant force can be obtained from the integral of the pressure distribution:

$$F = 2\pi \int_0^a Pr dr = 6\pi R^2 \left(1 - \frac{S}{H} \right) \frac{2\dot{S}}{S} \eta (1 - e^{-t/\lambda}) + 72\pi Bt\dot{S}^2 \eta e^{-t/\lambda} \quad (16)$$

where

$$B = \frac{3SR}{2(a^2 + 2SR)^4} \left[4a(SR)^{0.5}(3a^6 + 22a^4SR - 44a^2S^2R^2 - 24S^3R^3) - 3\sqrt{2}(2SR)^4 \right] \quad (17)$$

This may be generalized for a Maxwell fluid with multiple relaxation times by applying the linear superposition principle, thus

$$F = 6\pi R^2 \left(1 - \frac{S}{H} \right) \frac{2\dot{S}}{S} \sum_{i=1}^N \eta_i (1 - e^{-t/\lambda_i}) + 72\pi Bt\dot{S}^2 \sum_{i=1}^N \eta_i e^{-t/\lambda_i} \quad (18)$$

where N is the number of Maxwellian spring-dashpot elements in parallel, and the modulus of each element, G_i , is given by

$$G_i = \frac{\eta_i}{\lambda_i} \quad (19)$$

where η_i and λ_i are the viscosity and relaxation time of each element.⁴¹

The expression for the adhesion force can be derived for the current flow configuration by replacing the Newtonian viscous force in eq 5 with the viscoelastic force to give

$$F^* = \frac{k}{4\pi\sigma R} [Vt - (S - S_0)] = \left(1 - \frac{S}{H} \right) + \frac{3}{2\sigma} R \left(1 - \frac{S}{H} \right) \frac{2\dot{S}}{S} \sum_{i=1}^N \eta_i (1 - e^{-t/\lambda_i}) + \frac{18}{\sigma R} Bt\dot{S}^2 \sum_{i=1}^N \eta_i e^{-t/\lambda_i} - \frac{m\ddot{S}}{4\pi\sigma R} \quad (20)$$

This approximate solution captures the main features of the full solution such as stress overshoot and the associated transient decay, which could arise from the changing force applied to the sphere during separation. The fluid properties were calculated from measured rheological data (sections 3.1 and 4.1).

2.3. Capillary-Nonlinear Viscoelastic Model. In order to account for nonlinear viscoelastic behavior, it is necessary to determine the strain field in the liquid for the sphere-on-flat geometry that is generated during separation of the probe. Spiegelberg et al.³⁹ showed that the mean strain at the wall is an appropriate measure of the strain during the separation of parallel plates in the presence of a viscoelastic fluid, despite inhomogeneity in the strain field at the wall. Therefore, assuming a Newtonian velocity field (eq 12), the strain rate at the surface of the sphere, that is, when $z(r) = s(r)$, is as follows:

$$\dot{\gamma}[s(r)] = \frac{3r}{[s(r)]^2} \dot{s} \quad (21)$$

The mean strain rate is defined as

$$\dot{\gamma}_{av} = \frac{1}{\pi a^2} \int_0^a \int_0^{2\pi} \dot{\gamma}[s(r)] r d\theta dr = \frac{3\dot{S}}{(H - S)} \left[\frac{\sqrt{2R}}{\sqrt{S}} \tan^{-1} \left(\frac{a}{\sqrt{2SR}} \right) - \frac{a}{H} \right] \quad (22)$$

where θ is the azimuthal angle. Consequently, the mean strain, γ_{av} , may be obtained by integrating eq 22 with respect to time.

This result can then be substituted into the constitutive eq 9, while eq 23 is used to calculate the strain-dependent viscoelastic modulus of the liquid, $G(\omega, \gamma)$, where this modulus may be a transient or dynamic value at a fixed time or frequency, respectively:

$$G(\omega, \gamma) = G(\omega) h(\gamma) \quad (23)$$

where $h(\gamma)$ is described by a damping function of the following form:⁴²

$$h(\gamma) = \frac{1}{1 + \alpha\gamma^\beta} \quad (24)$$

where α and β are parameters fitted to the measured strain-dependent behavior of the liquid. This assumes that the effects of strain and strain rate are independent.

Hence, the constitutive eq 9, neglecting stress overshoot, can be written as

$$\tau = \frac{\dot{\gamma}(t)}{1 + \alpha\dot{\gamma}(t)^\beta} \sum_{i=1}^N \eta_i \left[1 - e^{-t/\lambda_i} \right] \quad (25)$$

Table 1. Properties of the PDMS Liquids, the Film Thicknesses, and the AFM Beam Stiffnesses for the Adhesion Measurements, the Range of Capillary Numbers Investigated, and the Calculated Maximum Contact Pressures

PDMS liquid	η_0 (Pa·s)	approx M_w (g/mol)	calcd R_g (nm)	Film thickness (nm)	cantilever stiffness, k (N/m)	Ca range	nominal maximum contact pressure, \bar{P} (kPa)
1	0.1	7000	5.4	890	12.95 ^a	3×10^{-7} – 5×10^{-4}	10.1
2	1	28 000	10.7	800	12.95 ^a	3×10^{-6} – 5×10^{-3}	11.3
3	10	60 000	15.7	1,600	12.95 ^a	3×10^{-5} – 5×10^{-2}	5.6
4	30	80 000	18.1	1,960	12.95 ^a	1×10^{-4} – 1×10^{-2}	4.6
5	105	120 000	22.2	276	27.8 ^b	5×10^{-4} – 5×10^{-2}	119.7
6	340	185 000	27.5	360	27.8 ^b	1×10^{-2} –1	90.9
7	1124	250 000	32.0	186	27.8 ^b	3×10^{-3} –2	180.9

^a Colloid probe radii: $R = 6 \mu\text{m}$. ^b Colloid probe radii: $R = 2.5 \mu\text{m}$.

An expression for the force can be derived in analogous way to eq 20:

$$F^* = \frac{k}{4\pi\sigma R} [Vt - (S - S_0)] = \left(1 - \frac{S}{H}\right) + \frac{3}{2\sigma} R \left(1 - \frac{S}{H}\right)^2 \frac{\dot{S}}{S} \left(\frac{1}{1 + \alpha\gamma(t)^\beta}\right) \sum_{i=1}^N \eta_i (1 - e^{-t/\lambda_i}) - \frac{m\ddot{S}}{4\pi\sigma R} \quad (26)$$

3. EXPERIMENTAL SECTION

3.1. Materials. The linear PDMS liquids were supplied by Dow Corning, U.K., and Wacker, Germany, and will be referred to as PDMS1–7 as denoted in Table 1, which summarizes the values of the zero shear rate viscosity, molecular weight, and radius of gyration; the nominal mean pressures applied in the dwell period (section 5.1) are also given. The surface tension for all the liquids was assumed to be 20.5 mN/m at a temperature of 20 °C,⁴³ which was the temperature at which the experiments were performed. The viscosities as a function of shear rate and oscillation frequency were measured using an AR 2000 rheometer (TA Instruments) with a cone and plate configuration operating at 20 °C. Stainless steel cones with diameters of 20 and 40 mm and angles of 4° and 2° were employed for the high and low viscosity liquids, respectively. The strain-dependent viscoelastic response of PDMS4–7 was assessed at an oscillation frequency of 1 Hz. The molecular weight of the liquids was estimated from the data presented by Lee et al.,⁴⁴ Mills,⁴⁵ and Rahalkar et al.,⁴⁶ while the radius of gyration of the molecules in the polymer melt was estimated using eq 27:^{47,48}

$$R_g \approx \kappa \left(\frac{M_w}{74}\right)^{0.5} \quad (27)$$

where $\kappa = 0.55$.

3.2. Spin Coating. PDMS1–4 were decanted onto clean Si wafers (IDB Technologies, U.K.; 2 nm native SiO₂ layer as determined by ellipsometry and described in section 3.3) and then spun at frequencies in excess of 30 Hz for various times, using a spin processor (WS-400 × 10^{−6}NPP-Lite, Laurell Technologies). The film thicknesses were controlled by varying the spin duration. PDMS5–7 were individually dissolved in HPLC grade toluene (Fisher Scientific, U.K.) to produce concentrations ranging from 0.2 to 3.0% w/w. The solutions were allowed to equilibrate for a minimum period of 48 h in order to ensure complete dissolution. A 50 μL droplet of solution was dispensed onto a clean Si wafer using a fixed needle syringe (Hamilton, U.K.) immediately prior to spin coating, yielding a thin film of PDMS liquid following evaporation of the solvent. The film thicknesses were controlled by varying the concentration of PDMS dissolved in the

solvent, and they were measured by ellipsometry as described in the next section.

In toluene, it was expected that the radius of gyration would be reduced compared to the pure liquids, since it is likely to be a poorer solvent. It was of interest to determine if the effect was sufficiently large to modify the morphology of the films deposited from this solvent. Consequently, dynamic light scattering was performed on 1.5% w/w solutions for all the PDMS liquids to assess the PDMS radius of gyration when dissolved in the solvent used for spin coating. Measurements were performed using a High Performance Particle Sizer (HPPS, Malvern Instruments, U.K.), which operates a laser with a wavelength of 632.8 nm. The refractive index of PDMS is 1.420 with an extinction coefficient of 0.001, as measured by spectroscopic ellipsometry (see section 3.3); the value for toluene (1.495) is a reference standard.

3.3. Ellipsometric Measurement of Film Thickness. Ellipsometry measurements were carried out using a UVISSEL spectroscopic ellipsometer (Jobin-Yvon/Horiba, U.K.) operating with DeltaPsi2 v2.0.8 software. The angle of incidence was set to 70°. The wavelength range for the incident light was 250–800 nm. Precautions were made to avoid performing measurements on visibly defective locations of the sample film. The spot size of the optical beam was approximately 2 mm². The determination of the film thickness was based on a four-phase ambient/PDMS/SiO₂/Si model, in which the PDMS liquid film was assumed to be isotropic and modeled as Lorentzian harmonic oscillator,⁴⁹ with an initial thickness that was varied using a multivariate iterative calculation procedure. Table 1 lists the thicknesses of the films used for the AFM measurements.

3.4. Atomic Force Microscopy Adhesion Force Measurements. Adhesion force measurements were performed using a Nano-Wizard II atomic force microscope (JPK, Germany) operating in contact mode under ambient conditions. This involved a scanner with a maximum lateral range of 100 × 100 μm and a maximum vertical range of 90 μm in conjunction with a CellHesion module (JPK, Germany). All sample handling was carried out using clean Dumostar tweezers (Agar Scientific, U.K.) to minimize the risk of sample contamination. Force measurements were performed using rectangular 90 μm length Si cantilevers (Novascan) with attached spherical SiO₂ colloid probes of diameters 2.5 and 6 μm. The cantilever spring constants, which were in the range 12–28 N/m, were determined according to the method described by Bowen et al.⁵⁰ and are listed in Table 1. The length and width of the beams were 90 and 35 μm, respectively. On this basis, the beam thicknesses were calculated to be 1.8 μm ($k = 12.95$ N/m) and 2.41 μm ($k = 27.8$ N/m). The beams were made from Si, which has a density of 2330 kg/m³ and a Young's modulus of 152 GPa. The probes were made from SiO₂, which has a density of 2200 kg/m³. The error in the spring constants was ±5%, calculated in accordance with the procedure outlined by Bowen et al.,⁵⁰ where the uncertainties were considered to be ±1 μm in the cantilever length and width,

± 10 Hz in the resonant frequency, ± 1 GPa in the Young's modulus, and ± 10 kg/m³ in the density.

The measurements were made by driving the fixed end of the cantilever at a specified velocity (the *drive velocity*) toward the sample surface, while monitoring the deflection of the free end of the cantilever using a laser beam. The drive velocity during the approach was maintained at a small value of 100 nm/s, in order to minimize viscous resistance to the colloid probe penetrating into the PDMS film. Following a dwell period of 120 s with a compressive force of 500 nN, the fixed end of the cantilever was retracted at drive velocities in the range 0.1–50 μ m/s and the deflection of the free end of the cantilever was again monitored. It was found that, for any given film, a dwell period of 120 s or greater yielded a constant maximum pull-off force during the retraction ramp at a given drive velocity, suggesting that the probe had reached a maximum penetration depth into the film for the given contact pressure. Therefore, the initial separation distance between the colloid probe and the counter-surface should have been approximately constant for each retraction drive velocity investigated. Real-time data traces were recorded for each measurement at an acquisition rate of 5 kHz. Subsequent analysis of the data allowed the distance traveled by the AFM probe tip through the PDMS film to be estimated, the thickness of which had previously been determined by ellipsometry. The peak retraction force was also obtained from the data; it is defined as that corresponding to the greatest attractive deflection of the free end of the cantilever.

3.5. Data Analysis. Matlab (MathWorks) was employed to solve eqs 5, 20, and 26 iteratively for S as a function of time using a numerical ordinary differential equation solver, ODE15s, to integrate the equation of motion. ODE15s is a variable order solver based on the numerical differentiation formula given by Shampine and Reichelt.⁵¹ It was used because the equation of motion is stiff, owing to possible oscillations in the solution, resulting in the more frequently used Runge–Kutta algorithms being computationally expensive. The evaluation of the equations requires the initial separation distance, S_0 , which could not be measured accurately, and the assumptions made in determining a value are discussed in section 5.1. On this basis, the maximum adhesion force was calculated for different values of the capillary number, Ca , which is defined as follows:

$$Ca = \frac{\eta_0 \dot{S}_{\text{peak}}}{\sigma} = \frac{\eta_0 V}{\sigma} \quad (28)$$

where \dot{S}_{peak} is the velocity corresponding to the maximum adhesion force when it is equal to that of the drive velocity during retraction (see section 4.3).

4. RESULTS

4.1. Rheometry. PDMS1–2 are Newtonian, which is consistent with their molecular weights being smaller than the critical entanglement value of 34 000 g mol^{−1} as specified by Dvornic et al.⁵² PDMS3–7 are viscoelastic, which is consistent with their molecular weights being greater than the critical entanglement molecular weight. Figure 2 shows the storage, G' , and loss moduli, G'' , as a function of frequency for (a) PDMS3 and (b) PDMS7 as examples. These parameters were fitted to a generalized Maxwell model:⁴¹

$$G'(\omega) = \sum_{i=1}^N \frac{\eta_i \lambda_i^2 \omega^2}{1 + (\lambda_i \omega)^2} \quad (29)$$

$$G''(\omega) = \sum_{i=1}^N \frac{\eta_i \lambda_i \omega}{1 + (\lambda_i \omega)^2} \quad (30)$$

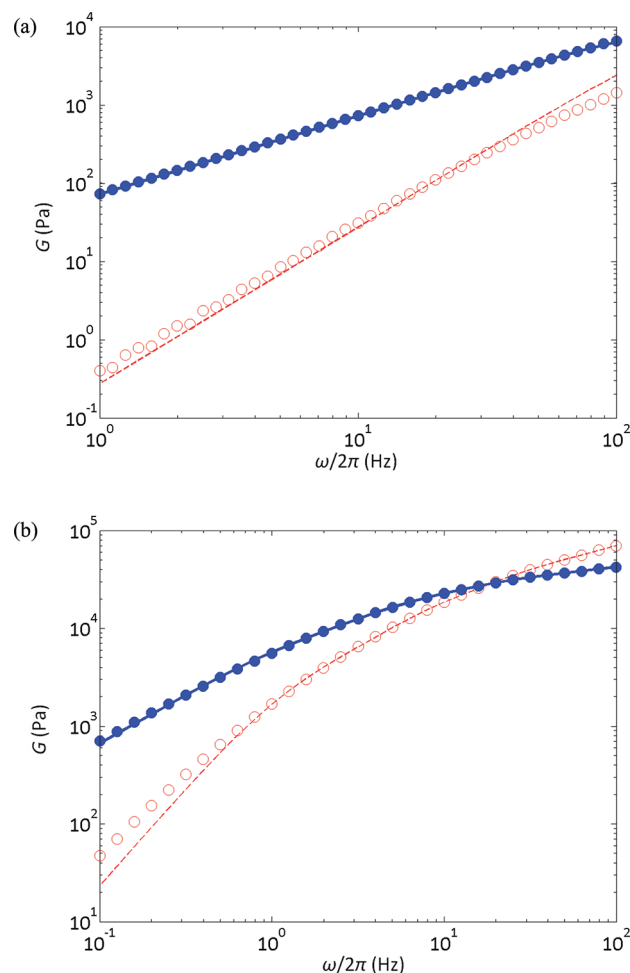


Figure 2. Measured storage (○) and loss (●) moduli of (a) PDMS3 ($\eta_0 = 10$ Pa·s) and (b) PDMS7 ($\eta_0 = 1,124$ Pa·s) as a function of the oscillation frequency. Dashed and continuous lines are the storage and loss moduli calculated using eqs 29 and 30.

where N is typically ≤ 4 for PDMS3–7. A series of moduli and relaxation times were calculated for each liquid using a least-squares method, which was based on comparing the calculated values, G'_j and G''_j , with those measured. The curve fitting was carried out using the Solver function in Microsoft Excel and involved minimizing the following expression:

$$\sum_{j=1}^M \left\{ \left[\frac{G'(\omega_j)}{G'_j} - 1 \right]^2 + \left[\frac{G''(\omega_j)}{G''_j} - 1 \right]^2 \right\} = \delta^2 \quad (31)$$

where δ is the sum of the errors for all j and M is the number of frequencies measured. Figure 2 also shows the curve fitting when eq 31 is applied to the measured storage and loss moduli of PDMS3, for which $N = 1$, and PDMS7, for which $N = 4$.

Figure 3 shows the master curves for G' and G'' based on the relationships described by Hadjistamov⁵³ in which these parameters are shown to scale with the product of the angular frequency, ω , and η . The master curves were used to calculate values of G' and G'' for frequencies outside of the experimentally accessible range.

Figure 4 shows the best fits of eq 24 to the rheometry data for PDMS5 and PDMS7. Table 2 lists the α and β parameters calculated for PDMS4–7 for use in eq 24, which describes the

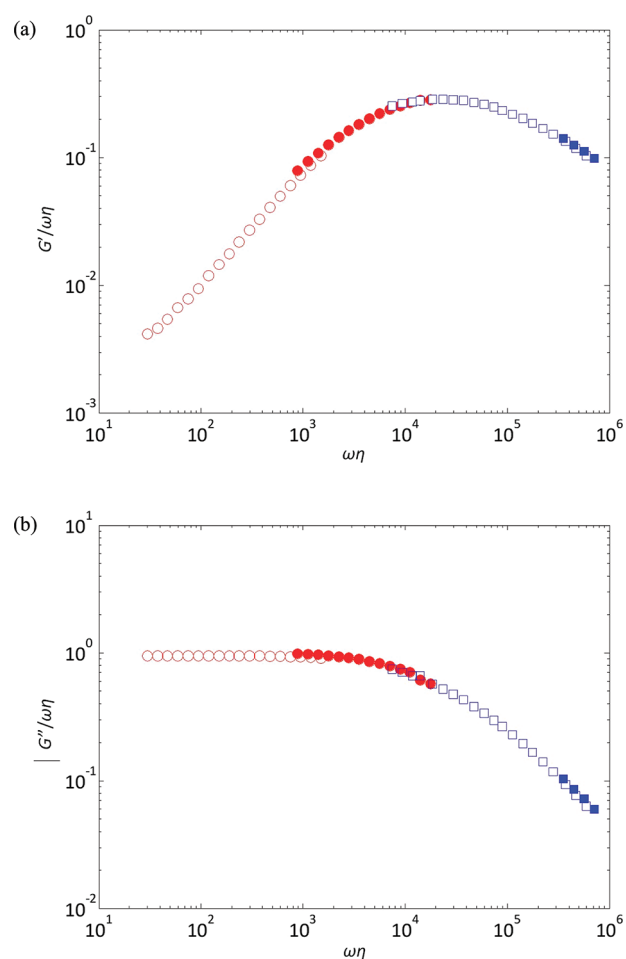


Figure 3. Master curves of (a) the storage modulus and (b) the loss modulus for PDMS calculated from the rheometry data for PDMS3 (○), PDMS4 (●), PDMS5 (□), and PDMS7 (■).

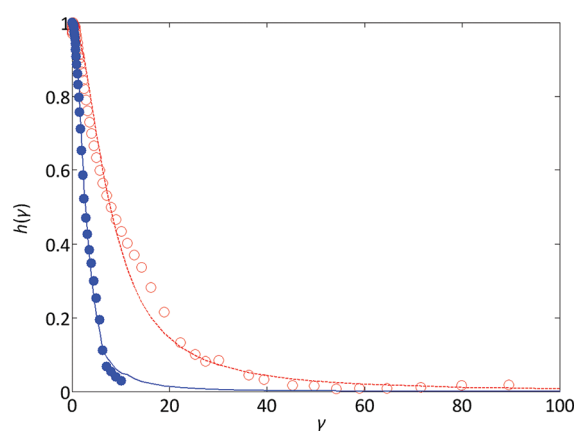


Figure 4. Measured damping function at 1 Hz as a function of the strain for PDMS5 (○) and PDMS7 (●); the lines are the best fit to eq 24.

strain-dependent modulus of the liquids. It should be noted that although PDMS3 exhibited weak viscoelastic behavior, the measurable strain dependency was negligible and hence $G(\omega, \gamma)$ was assumed to be equal to $G(\omega)$.

Table 2. Dtrain-Dependent Modulus Fitting Parameters (eq 24) for PDMS4–7

PDMS liquid	η_0 (Pa·s)	α	β
4	30	0.006	1.55
5	105	0.02	1.9
6	340	0.06	1.8
7	1124	0.1	2.2

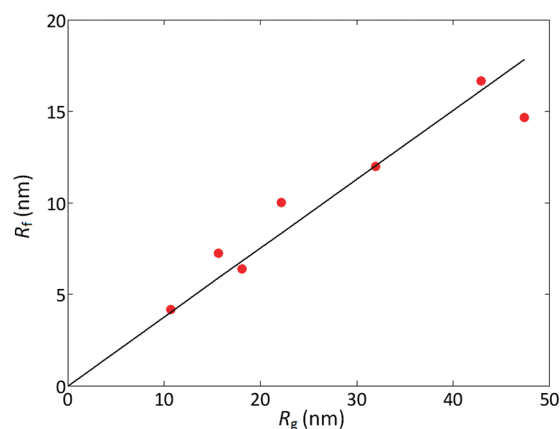


Figure 5. Flory radius for PDMS in toluenic solution as a function of the radius of gyration. The line is the best fit to the data ($R^2 = 0.817$).

4.2. Dynamic Light Scattering. Figure 5 is a plot of the measured Flory radius, R_f , as a function of the calculated radius of gyration, R_g , for PDMS1–7. The values of R_f are smaller than those of R_g and are linearly related within experimental error such that $R_f = \phi R_g$, where $\phi = 0.38$. That is, the PDMS liquid is a better solvent than toluene, as might be expected since the PDMS is essentially a theta solvent.

4.3. Atomic Force Microscopy. Figures 6 and 7 show typical force–distance data for an adhesion measurement performed with PDMS7 having a mean film thickness of 186 nm. The variability of all such data was less than 1%. The x -axis represents the distance of the fixed end of the cantilever from the minimum value corresponding to that at the completion of the dwell period. During approach, at a fixed-end displacement of 225 nm, an unstable jump can be seen due to the attractive potential acting between the probe and the surface of the liquid film, probably arising only from van der Waals interactions. On the basis of the change in the force and the stiffness of the cantilever, the displacement of the probe is 36 nm, giving a probe tip location that is approximately equal to the measured thickness of the film; the evidence suggests that a finite gap exists at the end of the dwell period (see section 5.1). There is a decrease in the probe velocity upon formation of a liquid junction between the probe and film, which occurs immediately after the jump-to event. Subsequently, the force remains constant for a limited period during which there is a balance between the opposing capillary and squeeze flow forces as the probe penetration depth increases. The force on the cantilever is tensile in this region of the force–displacement data, and hence, it can be considered that capillary forces dominate. Since the gradient in force is small, the velocity of the probe will be approximately equal to the drive velocity in this region. At longer times, the squeeze flow force becomes greater than the capillary forces and the resultant attractive force

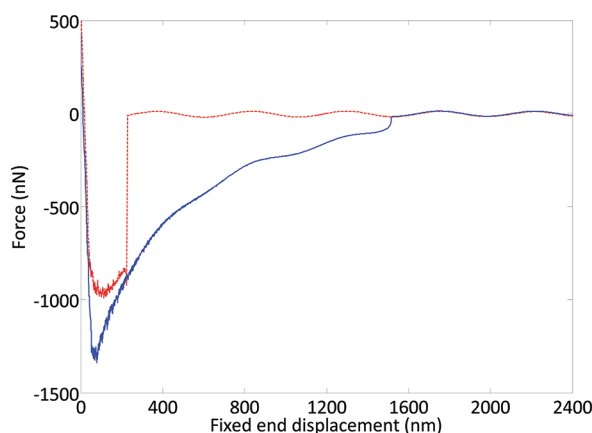


Figure 6. Measured AFM force–displacement curves for PDMS7 ($\eta_0 = 1,124 \text{ Pa}\cdot\text{s}$, $V = 100 \text{ nm/s}$, $H = 186 \text{ nm}$, $R = 2.5 \mu\text{m}$, $k = 27.8 \text{ N/m}$) showing data for the approach (dashed line) and retraction (continuous line).

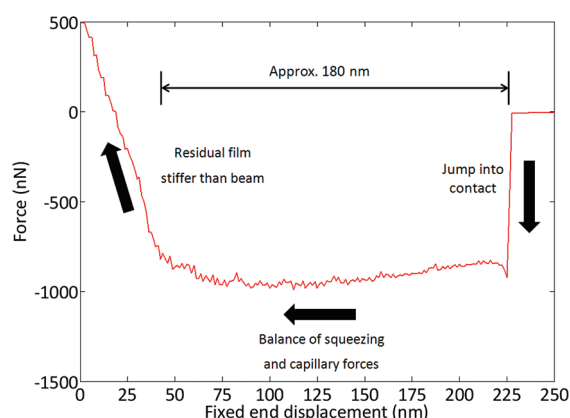


Figure 7. Details of the approach data shown in Figure 6.

acting on the probe starts to decrease until at 19 nm it has a zero value. At smaller values of the separation distance, there is an increase in the compressive force due to the squeeze flow resistance until a limiting minimum value of separation is reached corresponding to the stiffness of the residual liquid film being greater than that of the cantilever. It is not possible to measure directly the actual value of this minimum separation distance; its estimation is discussed in section 5.1.

Following the dwell period when retraction is initiated, the compressive load is removed and a tensile load is applied. The probe then starts to travel through the film, accelerating from a static state toward the drive velocity of the fixed end of the cantilever. The probe velocity becomes equal to the drive value at the peak force, since by definition this corresponds to the force gradient being zero; the finite time interval involved has been observed in previous work.⁵⁴ The tensile load applied to the probe upon retraction of the fixed-end subsequently decreases as it is driven further away from the film. The region of liquid in contact with the probe is deformed and pulled into a filament, which extends and thins as the probe is increasingly retracted. Finally, there is a rupture event, in this case at a fixed-end displacement of approximately $1.5 \mu\text{m}$.

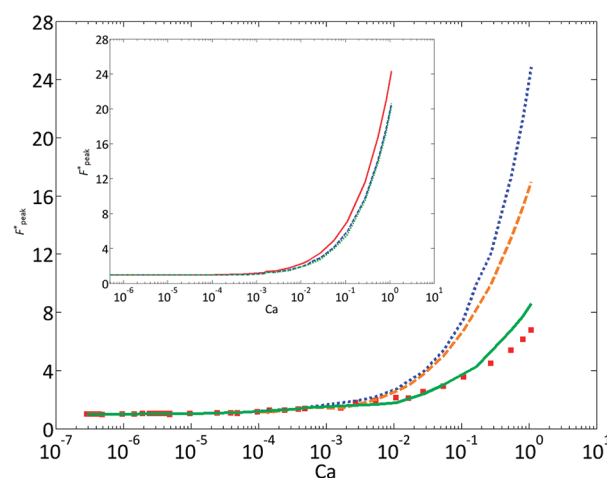


Figure 8. Measured values of the nondimensional adhesion force (\blacksquare), F_{peak}^* , as a function of the capillary number, Ca , together with the values calculated using the capillary-viscous model (continuous, eq 5), capillary-linear viscoelastic stress overshoot model (dashed, eq 20), and capillary-nonlinear viscoelastic model (dotted, eq 26). For $Ca < 10^{-4}$, the experimental and calculated data are approximately equal for all three models. Inset shows the effect of S_0 on F_{peak}^* (continuous, $S_0 = 5.6 \text{ nm}$; dashed $S_0 = 10 \text{ nm}$; dotted, $S_0 = 15 \text{ nm}$).

The measured peak adhesive force, F_{peak} , was normalized as follows:

$$F_{\text{peak}}^* = \frac{F_{\text{peak}}}{4\pi\sigma R} \quad (32)$$

Figure 8 shows that the measured value of F_{peak}^* is ~ 1 for $Ca < 10^{-3}$ and begins to increase gradually for $10^{-3} < Ca < 10^{-2}$, up to $F_{\text{peak}}^* \sim 9$ for $Ca \sim 1$. This represents a transition from the capillary plateau region where F_{peak}^* is independent of velocity to a region where the viscous or viscoelastic interactions are important.

It should be noted that optical interference is observable in the AFM data as an approximately sinusoidal low frequency signal. In Figure 6, it is most evident at larger separation distances but it actually occurs at all separation distances and is a significant factor in introducing uncertainties in the adhesion data (see section 5.4). The interference is caused by the reflection of the laser beam from both the AFM cantilever and the Si wafer. The wafers employed in this research were highly polished and therefore strongly reflective. They could not be substituted by a less reflective surface, such as glass, since the film thickness had to be ascertained by ellipsometry, which requires a reflective countersurface. Attempts were made to filter the interference by employing fast Fourier transforms (FFT), which has proven successful when applied to interference present in AFM images.⁵⁵ However, this proved to be unsuccessful when applied to the data obtained here, because the periodicity of the interference varied nonlinearly as a function of the separation distance. An atomic force microscope with high frequency current modulation was successful previously in minimizing the amplitude of interference in the acquired deflection signal,⁵⁶ but such equipment was not available for the experiments performed here.

4.4. Effect of Spin Coating from Solvent. It was important to establish whether the rheological properties of PDMS5–7 were affected by spin coating from toluenic solutions. Since PDMS5–7 could not be spin coated in a pure form in the same way as PDMS1–4, a 2.5% w/w toluenic solution of PDMS2 was created

and spin deposited onto a Si substrate. First, the ellipsometrically calculated properties of the PDMS2 film prepared from pure liquid and the film prepared from toluenic solution were compared over the wavelength range 300–800 nm. It was found that the refractive index and extinction coefficient for both films were identical within experimental error, suggesting that there was not residual toluene remaining in the film deposited from toluenic solution. Second, the peak adhesive force was measured for both PDMS2 films using AFM. At a drive velocity of 1 $\mu\text{m/s}$, the values of F_{peak}^* were 1.12 ± 0.06 and 1.08 ± 0.03 for the films prepared from the pure PDMS2 and from the toluenic solution. The corresponding values at a drive velocity of 10 $\mu\text{m/s}$ were 1.36 ± 0.14 and 1.35 ± 0.04 . Hence, there was no significant difference between the measured values for the two types of deposition.

5. DISCUSSION

5.1. Minimum Separation Distance. As discussed in section 4.3, it was not possible to directly measure the minimum separation distance in the current work, and this is a critical parameter for evaluating any theoretical models. It has been shown previously that thin films of polymer melts can exhibit different viscosities,^{57,58} diffusion coefficients,⁵⁹ and glass transition temperatures^{60,61} due to reduced chain mobility in the proximity of a liquid–solid interface. The reduction in chain mobility has been ascribed to steric hindrance, and the reduction is greater if there is an attractive interaction at the interface.⁶² As this is an interfacial phenomenon, the effect becomes less pronounced with increasing film thickness.⁵⁸ When the interaction is attractive, the resulting adsorption of the polymer chains at the interface⁶³ will cause a local increase in the viscosity. For repulsive interactions, the viscosity has been shown to decrease with respect to the bulk value as the film thickness is decreased.⁵⁸ For such systems, dewetting of the thin film can be imposed through the application of a surface perturbation.⁵⁸

In the current work, the above phenomena may have a significant effect on the minimum gap achieved between the colloid probe and the Si wafer. Previous work has revealed the presence of adsorbed layers of polymeric molecular chains aligned in a direction parallel to surfaces wetted by PDMS, due to attractive molecule–substrate interactions, using ellipsometry,⁶⁴ X-ray reflectivity,^{65,66} AFM,⁶⁷ and the surface forces apparatus (SFA).^{68–70} With the exception of the SFA experiments conducted by Yamada,⁷⁰ in which PDMS of molecular weight 80 kg/mol was studied, the values were in the range 3.5–6.5 kg/mol, corresponding to a viscosity of only $\sim 0.05 \text{ Pa}\cdot\text{s}$ or less. Hence, for the experiments conducted here, it can reasonably be expected that the colloid probe cannot penetrate completely through such films into direct contact with the wafer. From a comparison of the AFM approach curves with the ellipsometrically measured film thicknesses, it may be concluded that the probe travels through most of the film thickness before reaching a location close to the countersurface. For example, the approach curve shown in Figure 7 reveals that the probe has traveled approximately 180 nm when in contact with the liquid film, which is consistent with the ellipsometrically measured mean film thickness of 186 nm for this film, allowing for small fluctuations in film thickness across the substrate surface.

The presence of absorbed surface lubricating layers during AFM measurements has been proposed previously.⁷¹ The SiO_2 present at the colloid probe surface and the wafer will provide an

attractive potential that serves to flatten the random coil configurations of the PDMS molecules, forcing chains to lie parallel to the surfaces. Upon the approach of two mica surfaces in PDMS using SFA, the force between the plates was found to jump with a periodicity corresponding to 0.7 nm, the diameter of a PDMS chain,⁷⁰ when the separation distance between the surfaces was of the order of 5–6 nm.⁶⁸ The polymer chains are forced into a parallel configuration by the approaching plates such that these layers at the solid/liquid interface have a thickness of several nanometers. PDMS with molecular weights of 3.7 kg/mol⁶⁸ to 80 kg/mol⁷⁰ have been shown to produce a periodic layered structure when confined between two rigid interfaces. SFA experiments have shown that only with high contact pressures of $\sim 2 \text{ MPa}$ and with imposed lateral sliding can separation distances of the order of a few molecular layers be achieved.⁷⁰

In the current work, we assume that layering of the PDMS molecules will occur at the SiO_2 and Si surfaces regardless of the molecular weight of the PDMS employed. When the colloid probe is in contact with the film, the maximum mean contact pressure, \bar{P} , can be estimated using the following relationship:

$$\bar{P} = \frac{F_c}{\pi a^2} \quad (33)$$

where, F_c is the compressive load of 500 nN applied during the dwell period. The calculated values of \bar{P} are given in Table 1 and are approximately an order of magnitude smaller than 2 MPa. Therefore, it may be assumed that a separation distance of about 5–6 nm is appropriate for the experiments presented here. An initial separation distance of 5.6 nm is consistent with a 2.8 nm thickness layer present at both the wafer and probe surfaces, corresponding to eight molecular diameters of layered PDMS chains. The current data suggest that this separation distance is not a function of the molecular weight of the PDMS and, therefore, the radius of gyration. In the current analysis, it has been assumed that the flow properties at the minimum separation distance are equivalent to those of the bulk liquid. However, due to the acute radius of curvature of the probe, the separation distance increases rapidly with increasing radial distance and, moreover, the peak strain rate at the boundaries of the probe and wafer will be at some finite distance from the axis of symmetry.⁷²

5.2. Comparison of Experimental Results with the Capillary-Viscous Model. Figure 8 shows a comparison between the measured values of F_{peak}^* and those calculated using eq 5 for an initial gap of 5.6 nm. In the capillary regime ($\text{Ca} < 10^{-3}$), the measured values are comparable with those calculated using the capillary-viscous model with a negligible viscous component. The range $10^{-3} < \text{Ca} < 10^{-2}$ corresponds to the viscous regime when the force increases with increasing viscosity and separation velocity; these trends have been observed previously.^{27,29} In this range, the capillary-viscous model provides a satisfactorily accurate value of F_{peak}^* . At values of $\text{Ca} > 10^{-2}$, this model leads to an increasing overestimation of the measured forces; for example, for $\text{Ca} \sim 1$, the calculated value is approximately a factor of 4 greater than that measured. Such deviations could not be accounted for by uncertainties in the initial gap and the experimental data, and thus, the influence of a viscoelastic contribution was examined as discussed in the next section.

5.3. Comparison of Experimental Results with the Capillary-Linear Viscoelastic Stress Overshoot Model. Figure 8 shows that taking account of viscoelastic flow (eq 20) has reduced the calculated values of F_{peak}^* at the large values of Ca , leading to an improvement in the fit to the data. At $\text{Ca} \sim 1$, the measured

value of F_{peak}^* is ~ 6.8 , while the calculated values using the capillary-viscous and capillary-linear viscoelastic stress overshoot models are ~ 25 and ~ 15 , respectively. The stress overshoot term was found to be negligibly small, probably because of the square dependency of the probe velocity, and thus would be significant only at much greater velocities.

5.4. Comparison of Experimental Results with the Capillary-Nonlinear Viscoelastic Model. The calculated adhesive forces based on the capillary-nonlinear viscoelastic model (eq 26) are shown in Figure 8, and generally there is excellent agreement with the measured values but with some divergence for $Ca > 0.1$. For example, at $Ca \sim 1$, the measured value of F_{peak}^* is ~ 6.8 , while the calculated value using the nonlinear viscoelastic model is ~ 8.3 . This is significantly closer to the measured value than that calculated using the capillary-viscous model (~ 25) and the capillary-linear viscoelastic stress overshoot model (~ 15). For $Ca < 0.1$, there is close agreement between the measured and calculated values using the capillary-nonlinear viscoelastic model, which is a significant improvement on the other models, for which the deviation between measured and calculated values becomes evident at $Ca \sim 10^{-3}$.

It was concluded that the increasing deviation of the calculated values from the experimental data with increasing Ca for $Ca > 0.1$ is a result of the approximate nature of the theory. Further improvements based on analytical models to reduce the relatively small deviations in this range of Ca would be difficult, and consequently, it would be necessary to employ a numerical approach such as finite element analysis. Experimental errors, the uncertainty in estimating S_0 , and wall slip were considered as the main factors that could have contributed to the deviations; wall slip is discussed in section 5.5. The experimental data were extremely reproducible with deviations of $< 1\%$ for film thicknesses, forces, and viscosities measured using ellipsometry, AFM, and viscosities rheometry. The absolute uncertainty for ellipsometry was < 1 nm, while for the forces measured with the AFM it was $< \pm 15$ nN, which arises primarily from the optical interference. Since the amplitude of the interference was constant, it becomes increasingly insignificant with increasing Ca due to the increase in F_{peak} .

The calculated data were relatively insensitive to the absolute value of S_0 and the values of the separation distance, S_{peak} , corresponding to F_{peak} increased with Ca for $Ca > 10^{-3}$ and were more than an order of magnitude greater than S_0 at $Ca = 1$. Thus, in this range of Ca , the value of S_0 becomes an increasingly less significant factor, whereas the deviations from experiment of the calculated values of F_{peak} increase. The values of F_{peak} were calculated using the capillary-viscous model for values of S_0 of 5.6, 10, and 15 nm, which are shown in the inset in Figure 8. Increasing the value of S_0 in this range results in a relatively small reduction in F_{peak} that is insufficient to explain the deviations from the experimental data. Negligible differences were obtained for the corresponding calculations using the capillary-nonlinear viscoelastic model.

While the models are only applicable in the lubrication limit, it is useful for validation purposes to compare the directly measured and calculated forces as a function of time in this limit, which is exemplified for $Ca = 0.17$ in Figure 9. The capillary-viscous and capillary-linear viscoelastic stress overshoot models lead to large differences with the measured data. However, for the capillary-nonlinear viscoelastic model, there is a reasonable agreement with the measured value of F_{peak} and it corresponds to similar times. At greater times, the calculated force decreases

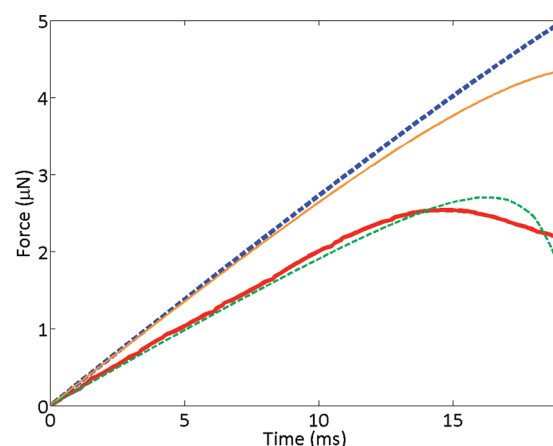


Figure 9. Measured force as a function of time (continuous thick line) and calculated values using the capillary-viscous model (dashed thick line, eq 5), capillary-linear viscoelastic stress overshoot model (continuous thin line, eq 20), and capillary-nonlinear viscoelastic model (dashed thin line, eq 26).

more rapidly than the measured force. It is reasonable to assume that the long wavelength optical interference (see section 4.3) is a significant factor in this deviation and is likely to contribute to the difference between the measured and calculated values of F_{peak} . The other contributory factor is that an extensional component to the flow field will become increasingly important with increasing separation distances.

5.5. The Effect of Slip. As discussed in section 5.1, the finite minimum gap, S_0 , probably arises from multimolecular layers in which the polymer chains are oriented in a direction that is parallel to the surfaces of the probe and wafer. Thus, there is some uncertainty about whether there could be slip between the bulk of the fluid and the adsorbed layer. The close agreement between the measured and calculated values of the force for the capillary-nonlinear viscoelastic model suggests that slip is not a significant factor. Moreover, recent experiments with PDMS liquids using AFM, in which slip was predicted and expected to be observed, proved not to be the case,⁷¹ leading to the conclusion that a no slip boundary condition was consistent with the Reynolds lubrication approximation. Following the same procedure as Vinogradova,⁷³ but using the boundary condition $\Delta P = 0$ at $r = a$, where ΔP is the difference between the hydrostatic pressure in the fluid and atmospheric pressure as assumed by Matthewson,³³ it may be shown that for a Newtonian liquid

$$\Delta P = \eta R \dot{S} \left\{ \frac{1}{6\xi} \left[\frac{1}{h(r)} - \frac{1}{H} \right] + \frac{1}{36\xi^2} \left[\ln \left(\frac{6\xi + H}{6\xi + h(r)} \right) - \ln \left(\frac{H}{h(r)} \right) \right] \right\} \quad (34)$$

where ξ is the slip length. Assuming that the parabolic approximation (eq 13) is valid, integration yields

$$F_{\text{V}}^* = \frac{\eta R \dot{S}}{2\sigma} \left\{ \frac{S-H}{\xi H} + \frac{6\xi + S}{6\xi^2} \left[\ln \left(\frac{6\xi + S}{6\xi + H} \right) + \ln \left(\frac{H}{S} \right) \right] \right\} \quad (35)$$

In the limit $\xi \rightarrow 0$, eq 35 reduces to eq 3, which was derived for a no slip boundary condition.

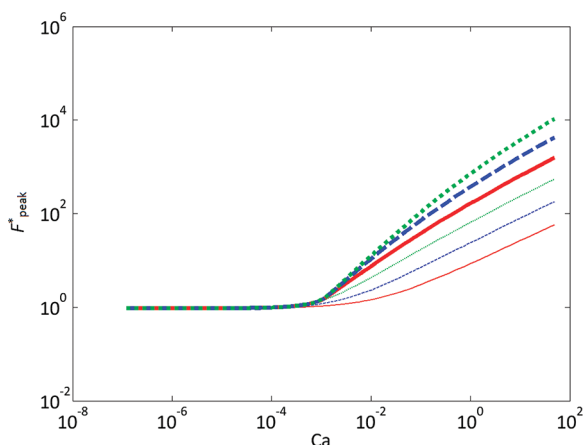


Figure 10. Effect of the cantilever spring constant, k , on the calculated values of the nondimensional adhesion force, F_{peak}^* , based on the capillary-viscous model (eq 5) where $k = 2$ (thin continuous), 2×10^1 (thin dashed), 2×10^2 (thin dotted), 2×10^3 (thick continuous), 2×10^4 (thick dashed), and 2×10^5 (thick dotted).

If a minimum gap of $S_0 = 0.2$ nm is assumed, which is consistent with the minimum possible gap allowing for interatomic repulsion, a slip length could be introduced that might account for the differences between the experimental and calculated peak forces. This corresponds to $\xi = 17.7$ nm, which is much greater than the upper bounds on the gap estimated from the experimental data. Moreover, although slip is predicted to occur when wetting is poor,⁷⁴ PDMS is perfectly wetting on SiO_2 surfaces, and hence Si surfaces, which generally have a native SiO_2 layer, and therefore this supports the contention that a no slip boundary condition is appropriate.

5.6. The Effect of Cantilever Spring Constant. It has previously been stated that the cantilever spring constant, or system stiffness, has an important effect on the magnitude of the forces measured during dynamic experiments such as those presented here.³⁴ All mechanical systems exhibit some form of compliance and hence can be considered to have a spring constant. For example, rigid-framed systems such as mechanical testers employ load cells that will have spring constants on the order 10^5 N/m and greater. Additionally, AFM cantilevers made from photocurable resin have been manufactured using Direct Digital Manufacturing,⁷⁵ exhibiting spring constants of the order 100–1000 N/m, which allows beams in the μN to mN force regimes to be used in AFM. Hence, F_{peak}^* was calculated as a function of Ca for different values of k using both the capillary-viscous and capillary-nonlinear viscoelastic models. The results are shown in Figures 10 and 11, respectively. For these calculations, $H = 500$ nm, $\sigma = 20.5$ mN/m, and $R = 5$ μm . Figure 10 shows that increasing k does not significantly influence F_{peak}^* for $\text{Ca} < 10^{-4}$, but for $\text{Ca} > 10^{-4}$ there is a pronounced dependency on k with the effect becoming greater with increasing k . For $\text{Ca} = 10$ and $k = 2$ N/m, $F_{\text{peak}}^* = 22.8$, and for each order of magnitude increase in k , up to $F_{\text{peak}}^* = 3683$ for $k = 2 \times 10^5$ N/m, F_{peak}^* is increased by a factor of 2 or more. These results demonstrate that, for Newtonian liquids, the stiffness of a mechanical system will have a significant effect on the probe velocity upon retraction and therefore the measured value of F_{peak}^* . Figure 11 shows that for viscoelastic liquids the effect of k on F_{peak}^* also becomes apparent for $\text{Ca} > 10^{-4}$. However, the results for 200 N/m $< k < 2 \times 10^5$ N/m have a similar value in the range $10^{-3} < \text{Ca} < 0.1$.

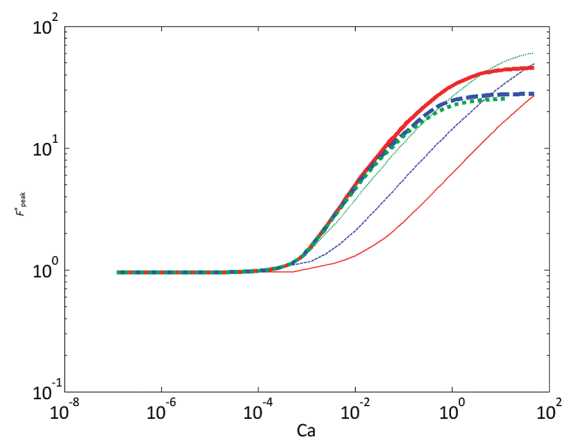


Figure 11. Effect of the cantilever spring constant, k , on the calculated values of the nondimensional adhesion force, F_{peak}^* , based on the capillary-nonlinear viscoelastic model (eq 26) where $k = 2$ (thin continuous), 2×10^1 (thin dashed), 2×10^2 (thin dotted), 2×10^3 (thick continuous), 2×10^4 (thick dashed), and 2×10^5 (thick dotted).

For $\text{Ca} > 0.1$, greater values of k start to yield smaller values of F_{peak}^* , which suggests that the viscoelastic response of the liquid is extremely sensitive to k . The Supporting Information contains details regarding numerical oscillations that tended to occur during the calculation of peak forces under these conditions, at the onset of probe motion. It is not possible to deduce whether the oscillations are a numerical artifact since none were observed experimentally, but the stiffnesses involved were much lower.

6. CONCLUSIONS

The current work has established that an AFM in conjunction with a colloid probe is suitable for characterizing the adhesive behavior of thin films of PDMS liquids spin coated onto Si wafers. Even for slow approach velocities and long dwell times, the minimum separation distance between the probe and the wafer was assumed to be ~ 6 nm irrespective of the molecular weight and hence the radius of gyration in the bulk fluid; this distance corresponds to a multimolecular layer in which the polymer chains are oriented in a parallel direction to the surfaces of the probe and wafer. Analytical models can be derived to estimate the maximum adhesive force as a function of the Capillary number, Ca . For small values of Ca , the data are consistent with those calculated on the basis of the capillary forces. There is a lower critical value of Ca above which viscous forces also become significant and the measured adhesive forces may be accurately calculated on this basis. For viscoelastic liquids at larger values of Ca , these calculated values of the force increasingly overestimate those measured. To a reasonable approximation, this may be accounted for at $\text{Ca} > 0.1$ by considering the influence of nonlinear viscoelasticity. The inertia of the AFM beam and viscoelastic stress overshoot effects were negligibly small and thus were not contributory factors. Finally, it was observed that the maximum viscous/viscoelastic adhesive force increases as the stiffness of the beam increases.

■ ASSOCIATED CONTENT

Supporting Information. Discussion of the system oscillations during AFM pull-off simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: m.j.adams@bham.ac.uk. Telephone: + 44 (0) 121 414 5297. Fax: +44 (0) 121 414 5377.

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